A New Method for Estimation of Activation Energies Associated with Coal Gasification Reactions

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Kinetic studies of coal gasification and pyrolysis are important in the design and operation of gasification plants. In many of these studies, weight loss of a coal sample is continuously recorded, with a TGA for example, to produce conversion versus time data for a specific set of experimental conditions. Theoretical and empirical models are frequently used to represent those primary kinetic data. With a proper representation of the conversion data, other secondary kinetic data such as half-life and reactivity are evaluated. Characterization of coal, development of proper reaction rate models and estimation of its activation energy follow.

Mahajan et al. (1978) found that when the char conversion is plotted as a function of a dimensionless time τ, defined by $\tau = t/t_{1/2}$, where $t_{1/2}$ is the half-life of the reaction, gasification data for widely different experimental conditions can be represented by a single x versus τ curve. This unification approach has been used and confirmed by a number of researchers, e.g., Kasaoka et al. (1985) and Peng et al. (1986).

In this work we use the unification approach as the basis to develop a theoretical relation between half-life and average reactivity which is then verified experimentally. The relation in turn leads to the development of a simple and practical alternative for estimating the apparent activation energies of coal gasification and other types of reactions.

THEORY

Char conversion x depends on experimental variables such as temperature, pressure, etc., and it increases with gasification time. This may be represented symbolically as

$$x = f_o\ (T,\ P,\ \ldots\ ,\ t) \qquad (1)$$

For each gasification run, with variables other than t being fixed, researchers usually fit to the conversion-versus-time data rate expressions of the form

$$R_C = dx/dt = F(x) \qquad (2)$$

where R_C is the char reactivity and x the char conversion.

According to the unification approach, when the data sets are normalized by replacing t by τ, a single x versus τ curve represents all the data, irrespective of the other experimental variables, reacting media and coal types. In other words, Eq. (1) becomes

$$x = f(\tau), \tag{3}$$

where f is the functional form of the unification curve. In this article, we show that this curve can be reduced even further, into a universal value, through the following discussion:

Eq. (3) may alternatively be presented as

$$\tau = g(x). \tag{4}$$

The above two equations are mathematical statements of the unification concept. From both equations,

$$dx/d\tau = f'(\tau) = f'\{g(x)\} = G(x) \tag{5}$$

Thus, $dx/d\tau$, the normalized reactivity is a function of conversion alone, and by averaging this reactivity over the entire conversion range, we remove the dependence of the normalized curve on conversion as well. Hence, if we define average normalized reactivity R_u as

$$R_u = \overline{dx/d\tau} = \frac{\int_0^1 (dx/d\tau)dx}{\int_0^1 dx} = \int_0^1 (dx/d\tau)dx = \int_0^1 G(x)dx \tag{6}$$

then, R_u is a universal constant.

Similar to Eq. (6), the average reactivity for a particular gasification run $\bar{R}_c$, is

$$\bar{R}_c = \overline{dx/dt} = \int_0^1 (dx/dt)dx = \int_0^1 F(x)dx \tag{7}$$

which, as shown above, is a constant quantity unique to each run. Thus, from Eqs. (6)-(7) and the definition of τ,

$$t_{1/2}\bar{R}_c = R_u \tag{8}$$

Therefore, we have obtained a simple relation which states that $\bar{R}_c$ is inversely proportional to $t_{1/2}$ with R_u as the proportionality constant.

In the kinetic studies of coal gasification and pyrolysis, often the activation energy is estimated from an Arrhenius plot of initial reactivity R_{co}, i.e., the reactivity at zero conversion, or half-life reactivity $R_{c,1/2}$, i.e., reactivity at 50% conversion. In some cases, rate constants k are obtained by fitting a model to the data, and activation energy estimated from an Arrhenius plot of the rate constants. Here, instead, let us define an average activation energy $\bar{E}_c$ based on $\bar{R}_c$ by the following Arrhenius relation:

$$\bar{R}_c = A \exp(-\bar{E}_c/RT) \tag{9}$$

This, when combined with Eq. (8), can be rearranged to get

$$t_{1/2} = (R_u/A)\ \exp(\bar{E}_c/RT) \qquad (10)$$

Hence a plot of $\ln(t_{1/2})$ versus (1/T) should yield a straight line with a slope equal to $\bar{E}_c/R$. In other words, Eq. (10) provides a simple means of estimating $\bar{E}_c$ directly from the $t_{1/2}$ data alone.

EXPERIMENTAL

Kinetic studies of char-steam reaction of North Dakota lignite were conducted with a TGA apparatus (Peng et al., 1986) at pressures 1 atm and 7.8 atm, in the temperature range of 800 to 1200°C. The mean particle size of the coal sample was 178 microns and steam was in excess. The chars were generated "in-situ" by devolatilization in a steam-nitrogen atmosphere, and gasified in the same environment without interruption (Peng et al., 1986). The reaction was allowed to go to completion. The weight loss of the sample was continuously recorded on a microcomputer and analyzed. More details of our study will be available later (Raghunathan).

RESULTS AND DISCUSSION

Conversion versus time data were obtained for eleven gasification runs at both pressures. The data are plotted as x versus τ in Fig. 1 and the unification approach is seen to be valid for our data. For each of these runs, various two-parameter rate models from literature (Johnson, 1979; Simons, 1979; Bhatia & Perlmutter, 1980; Gavalas, 1980; Kasaoka et al., 1985) are fitted, and from the model that best fits the data, $\bar{R}_c$ is calculated. Using those average reactivity data, we have plotted $(1/\bar{R}_c)$ versus $t_{1/2}$ in Fig. 2. Remarkably, they form a near perfect straight line passing through the origin with a correlation coefficient of 0.997 when fitted by the method of least squares, thus confirming the relation represented by Eq. (8). From the slope, the value of R_u is 0.385.

In Fig. 3, $\ln(t_{1/2})$ and $\ln(\bar{R}_c)$ are plotted versus (1/T) for both pressures. At 1 atm, the plots are linear over the entire temperature range, and, when calculated from the slope, the $\bar{R}_c$ values yield 61.1 kJ/mole for $\bar{E}_c$, whereas from the $t_{1/2}$ data, $\bar{E}_c$ is 62.8 kJ/mole. Clearly the values are very close. For the same runs, Arrhenius plots of R_{co} and $R_{c,1/2}$ yield activation energies of 64.5 and 60.8 kJ/mole, respectively.

For our experiments at 7.8 atm, the Arrhenius plot of average reactivity in Fig. 3 indicates the presence of two different controlling regimes: (1) between 1000°C and 1200°C, where the activation energy is nearly zero and (2) between 800°C and 1000°C, where a non-zero activation energy can be defined. The half-life data plotted in the same figure is seen to indicate this trend just as well. At this pressure, in the temperature range 800-1000°C, the $\bar{R}_c$ values yield 43.6 kJ/mole for $\bar{E}_c$, and the $t_{1/2}$ values yield 43.0 kJ/mole. Again, the values are close. From the R_{co} and $R_{c,1/2}$ values, the activation energies estimated are 44.4 and 43.5 kJ/mole, respectively. Discussions about the type of controlling mechanisms involved are beyond the scope of this article, and will be reported elsewhere.

Our results clearly indicate that, from the half-life data alone, (1) if there is a shift in the controlling mechanism in the temperature range, it can be detected by our method as well, and (2) the corresponding activation energy can also be estimated with reasonable accuracy.

Activation energy values are reported in literature for various gasification systems, evaluated through different methods. We have used the above approach to calculate the $\bar{E}_c$ values from their half-life data alone and Table 1 shows the comparison. We did not test the validity of unification theory or Eq. (8) with their data, but the $\bar{E}_c$ values so obtained are in good agreement with their reported values of activation energy. It is worth noting that the literature data shown in the table cover a wide variety of chars and represent different methods of estimating activation energy.

Hence, our results indicate that half-life data at different temperatures alone are sufficient to estimate the apparent activation energy of coal gasification reactions. This would eliminate the usually tedious and inaccurate procedures of evaluating the derivative of x(t) associated with the estimation of reactivity and thus activation energy. Although experimental verification is based on coal gasification reactions, this method is expected to be applicable to other types of gas-solid reactions, e.g., oil shales retorting, and is certainly applicable to any reaction systems which satisfy the unification theory represented by Eqs. (3) and (4).

ACKNOWLEDGEMENT

This work was supported in part by the Department of Energy under Contract AC21-83MC20320. We thank I. C. Lee for helping with the experiments.

NOTATION

A	preexponential factor in Arrhenius relation
$\bar{E}_c$	average activation energy
$f'(\tau)$	$df(\tau)/d\tau$
k	rate constant
R_c	char reactivity
R_{co}	initial reactivity
$R_{c,1/2}$	half-life reactivity
$\bar{R}_c$	average char reactivity
R_u	average normalized char reactivity, a universal constant

t	time
$t_{1/2}$	half-life of a reaction
T	reaction temperature
x	char conversion
τ	normalized time, $t/t_{1/2}$

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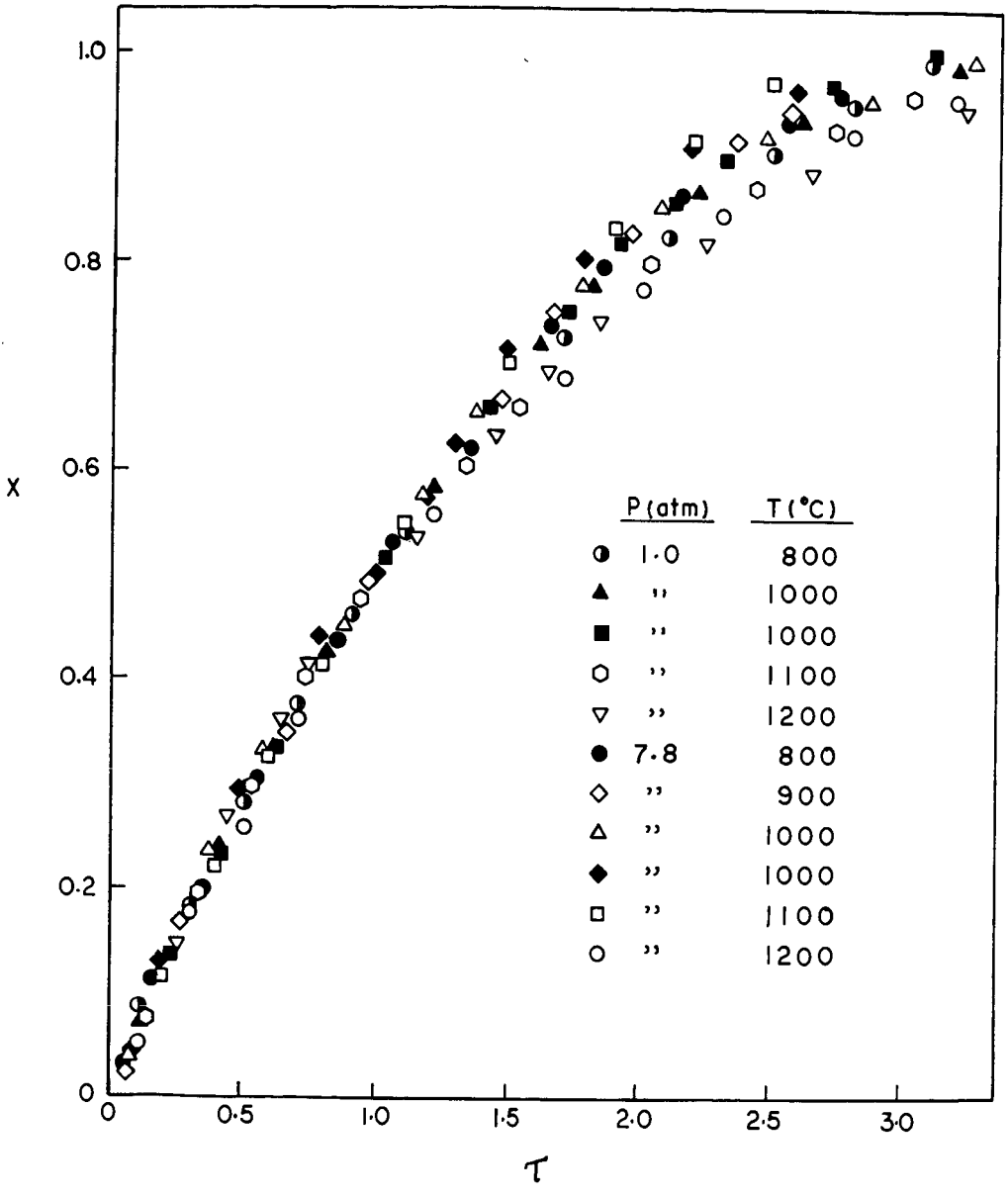
Table 1

Source	Char	Medium	Activ. Energy (kJ/mol) from R_{co}	$R_{c,1/2}$	k	$t_{1/2}$
Our Data	lignite	steam	64.5	60.8	---	62.8
	lignite	steam	44.4	43.5	---	43.0
Peng et al. (1986)	bitum.	steam	56.8	36.5	---	43.9
	subbitum.	steam	60.6	57.2	---	61.7
	lignite	steam	84.7	79.7	---	91.1
	bitum.	steam	62.6	47.6	---	48.4
	subbitum.	steam	82.4	54.1	---	55.8
	lignite	steam	98.5	67.4	---	75.1
Debelak et al. (1984)	subbitum.	CO_2	---	---	150.0	158.6
Chin et al. (1983)	brown coal activ. C	steam	---	---	125.6	129.4
	bitum. activ. C	steam	---	---	149.1	149.5
Schmal et al. (1982)	subbitum.	steam	---	---	165.4	161.6
Schmal et al. (1983)	subbitum.	steam	---	---	163.3	147.4
Guzman and Wolf (1982)	catalyzed activ. C	steam	---	---	259.6	250.7
	catalyzed bitum.	steam	---	---	242.8	239.8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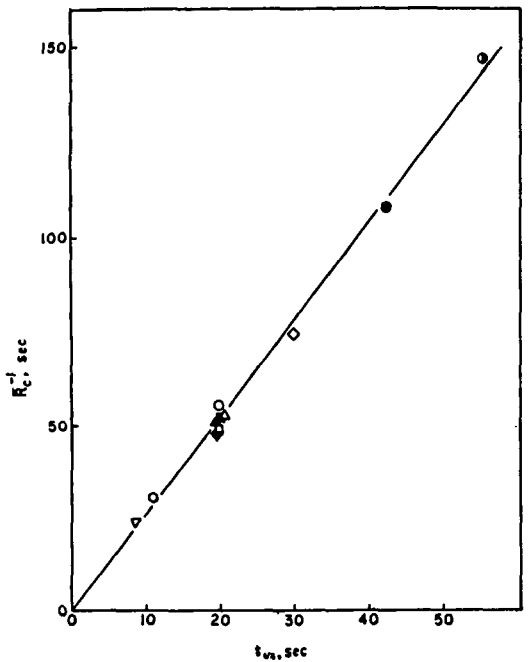

Figure 2. Reciprocal Average Reactivity versus Half-life

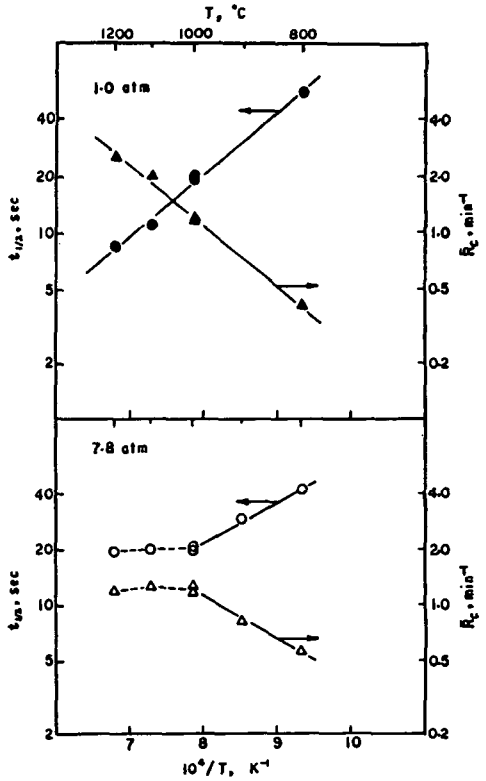

Figure 3. Comparison of Arrhenius Plots of Average Reactivity and Half-life at 1.0 and 7.8 atm.